

# APPLICATION FOR UNITED STATES LETTERS PATENT

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TITLE: METAL DEPOSITION PROCESS WITH  
PRE-CLEANING BEFORE  
ELECTROCHEMICAL DEPOSITION

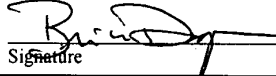
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METAL DEPOSITION PROCESS WITH PRE-CLEANING BEFORE  
ELECTROCHEMICAL DEPOSITION

5           The present application claims priority from U.S.  
Provisional Patent Application Serial No. 60/415,242, filed  
October 1, 2002, which is hereby incorporated by reference  
herein in its entirety.

10   FIELD OF THE INVENTION

This invention is concerned with semiconductor  
device manufacturing and is more particularly directed to a  
metal deposition process with pre-cleaning before  
electrochemical deposition.

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BACKGROUND OF THE INVENTION

A common process sequence in manufacturing  
integrated circuits and other electronic devices is to form  
a pattern of metal conductors on a substrate, then cover the  
20 metal conductors with a dielectric layer, and etch a number  
of openings in the dielectric layer so that each opening  
exposes a contact area on underlying metal conductors. A  
metal plug may be deposited in each opening so as to permit  
electrical contact between the underlying metal conductors  
25 and another metal layer to be deposited on the dielectric  
layer. Increasingly, copper is the metal used for such  
above-described metal layers, because of its relatively low  
resistivity.

Because of the tendency of copper to diffuse into  
30 dielectric layers, it is conventional to deposit a barrier  
layer on a dielectric layer and in its contact openings  
(which are also referred to as "vias" if the contact is to a  
lower metal layer) prior to forming a copper metal layer  
over the dielectric layer. A copper seed layer typically is  
35 deposited on the barrier layer, by a process such as

physical vapor deposition (PVD); and electrochemical deposition (ECD) such as electrochemical plating (ECP) is employed to fill each via (e.g., using a copper fill layer).

In conventional copper or other metallization processes, the metal fill layer may have defects such as voids, craters, carbon defects, pea-pods and the like. Surface defects such as particles, pea-pods and stains often can be removed by processes performed after ECD, such as by chemical-mechanical polishing (CMP). However, voids cannot be removed by post-ECD polishing, and may cause damage to devices that are formed on the substrate.

Voids in a copper fill layer may be the result of contamination on the copper seed layer employed prior to ECD. One source of contamination may be vacuum grease from the chamber in which the copper seed layer deposition process was performed. Also, contamination from airborne organic material may occur while a substrate is being stored after copper seed layer deposition and before ECD. Other possible sources of contamination include cassettes or other containers in which the substrate is stored, and devices which handle the substrate. Even though substrates are typically stored in clean rooms, in which airborne contaminants are minimized, it is still the case that the longer the storage period between copper seed layer deposition and ECD, the larger the potential for copper seed layer contamination.

The presence of organics and other contaminants on a copper seed layer may interfere with wetting of the copper seed layer by an electrolyte during ECD. For example, the rate of copper deposition during ECD at contaminated areas may be low (or no nonexistent), resulting in voids in those areas. It would therefore be desirable to provide a metallization process which reduces or eliminates sources of voids, in order to increase device yield.

The formation of air bubbles or air pockets that may contact the surface of a copper seed layer of a substrate during immersion of the substrate in the electrolyte solution of an ECD bath may be problematic. For example, air bubbles may cause pitting, tarnishing, deformations, and/or non-uniformity of the deposited layer, and if present for a sufficient time, may inhibit the capacity of metal ions in the electrolyte solution to deposit on a substrate, thereby creating a void in the deposited layer. Formation of such air bubbles or air pockets may be triggered by the presence of organic and other contaminants.

Another problem that may be encountered as a result of transporting a substrate from a seed layer deposition location to an ECD location, and/or as a result of storing the substrate between seed layer deposition and ECD, may be growth of a copper oxide layer on the seed layer. For example, if copper oxide were left on a copper seed layer and ECD copper fill was performed on top of the copper oxide layer, the resistivity of the resulting contact may increase.

It would therefore be desirable to provide inexpensive and efficient techniques for eliminating oxide layers, contaminants and the like from a metal seed layer prior to fill layer deposition, as well as to provide inexpensive and efficient techniques for generally limiting the potential for air bubbles to be formed on a seed layer via immersion of the substrate in an electrolyte solution of an ECD bath.

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#### SUMMARY OF THE INVENTION

According to a first aspect of the invention, a method includes providing a substrate having a metal seed layer, and applying an agitated rinse to the metal seed layer. The method according to the first aspect of the

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invention also includes depositing a metal fill layer on the rinsed metal seed layer by electrochemical deposition.

As used herein and in the appended claims, the term "agitated rinse" includes exposing an object to a liquid while (1) spraying the liquid on the object with a nozzle, a jet and/or a similar device that increases the speed and/or pressure of the liquid; (2) rotating and/or vibrating and/or otherwise agitating the object; and/or (3) applying megasonic and/or ultrasonic energy and/or other agitation to the liquid. Such agitated rinsing may, for example, break adhesive forces between contaminants and a substrate.

According to a second aspect of the invention, a method includes providing a substrate having a metal seed layer, and exposing the metal seed layer to a liquid that includes a surfactant. The method according to the second aspect of the invention further includes depositing a metal fill layer on the metal seed layer by electrochemical deposition.

According to a third aspect of the invention, a method includes providing a substrate having a metal seed layer, and exposing the metal seed layer to an organic solvent. The method according to the third aspect of the invention further includes depositing a metal fill layer on the metal seed layer by electrochemical deposition.

According to a fourth aspect of the invention, a method includes providing a substrate having a metal seed layer, and exposing the metal seed layer to activated hydrogen at a pressure of at least 0.1 atmosphere. The method according to the fourth aspect of the invention further includes depositing a metal fill layer on the metal seed layer by electrochemical deposition. Activated oxygen may be alternatively or additionally employed.

As used herein and in the appended claims, hydrogen is "activated" when it is at any level above the

ground state or is missing an electron. Hydrogen in plasma form is "activated". A "plasma" should be understood to include a glow discharge or the like.

According to a fifth aspect of the invention, a  
5 method includes, providing a substrate having a metal seed layer, and exposing the metal seed layer to an oxidant solution so as to form an oxidized surface layer on the metal seed layer. The method according to the fifth aspect of the invention further includes depositing a metal fill  
10 layer on the metal seed layer by electrochemical deposition.

By applying a liquid pre-clean to a metal seed layer in accordance with one or more of the first three aspects of the invention, organic and/or other contaminants on the metal seed layer may be reduced or eliminated,  
15 thereby improving wettability of the seed layer and promoting more effective electrochemical deposition at the metal fill stage. Void defect formation may be reduced and device yield may be increased.

The relatively high pressure reduction of metal  
20 oxide on a seed layer by means of activated hydrogen in accordance with the fourth aspect of the invention may both eliminate organic and/or other seed layer contamination, with the advantages described above, while also eliminating a metal oxide layer without significantly reducing the  
25 thickness of the metal seed layer. Moreover, the relatively high-pressure process of the fourth aspect of the invention may be performed inexpensively and efficiently (e.g., without requiring the use of a vacuum chamber).

Other objects, features and advantages of the  
30 present invention will become more fully apparent from the following detailed description, the appended claims and the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow chart that represents a metallization process performed in accordance with the present invention;

FIG. 2 is a schematic side view of a conventional megasonic tank that may be employed in the pre-clean step of FIG. 1;

FIG. 3 is a schematic perspective view of an apparatus that may be employed in an alternative embodiment of the pre-clean step of FIG. 1;

FIG. 4 is a schematic top plan view of an apparatus provided in accordance with the invention and in which both the pre-clean and ECD steps of FIG. 1 may be performed; and

FIG. 5 is a schematic cross-sectional view of an apparatus which may be employed for still another embodiment of the pre-clean step of FIG. 1.

#### DETAILED DESCRIPTION

According to various aspects of the invention, a metal seed layer such as a copper seed layer is cleaned before electrochemical deposition (ECD) of a metal fill layer. The "pre-clean" may be by either a liquid pre-clean, or by exposing the seed layer to activated hydrogen and/or oxygen, to remove contaminants and/or chemically reduce an oxide of the seed layer. In one or more embodiments, the pre-clean may include one or more of agitation of a rinsing liquid, inclusion of a surfactant in the rinsing liquid, use of an organic solvent. Alternatively, or additionally, a metal seed layer may be exposed to a solution containing an oxidant prior to formation of the metal fill layer (e.g. to increase wettability of the metal seed layer upon immersion in an electroplating solution).

FIG. 1 is a flow chart that illustrates an exemplary metallization process performed in accordance with the present invention.

FIG. 1 begins with a step 101, at which a metal seed layer, such as a copper seed layer, is deposited on a substrate. The substrate may be, for example, a silicon wafer or other type of other semiconductor wafer, or a glass plate. Step 101 may be performed in accordance with conventional practices. For example, step 101 may represent physical vapor deposition (also referred to as "sputter deposition") of a copper seed layer on a silicon wafer upon which a barrier layer has previously been deposited. The substrate may include features such as vias (e.g., in a dielectric layer) which provide access to an underlying metallization layer or to active regions of the semiconductor material. Exemplary barrier layers include tantalum, tungsten, titanium and/or nitrides thereof. Other seed layer deposition techniques may be employed such as chemical vapor deposition or atomic layer deposition.

Step 103 follows step 101 and represents a pre-cleaning step that is applied to the metal seed layer in accordance with the invention. Details of step 103 are provided below. The pre-cleaning step 103 may be performed after a period during which the substrate (having the metal seed layer deposited thereon) has been stored. Such a period of storage may, for example, last several days or more. Alternatively, the pre-cleaning step 103 may be performed immediately after step 101.

Following step 103 is step 105. At step 105 a metal fill layer is deposited on the pre-cleaned metal seed layer via electrochemical deposition (e.g., electrochemical plating). Step 105 may be performed in accordance with conventional practices, and, because of the inventive pre-cleaning of step 103, may produce fewer void defects than conventional metallization processes. Step 105 preferably is performed immediately following step 103 to prevent recontamination and/or oxidation of the metal seed layer.



Details of the inventive pre-cleaning step 103 will now be described.

The pre-cleaning step 103 may include, for example, dipping the substrate in a pre-cleaning liquid bath and/or holding the substrate in the bath for a predetermined period of time. In addition, or alternatively, the pre-cleaning step 103 may include spraying a pre-cleaning liquid on the substrate (e.g., on the metal seed layer). The substrate may be vibrated and/or rotated and/or otherwise agitated while the pre-cleaning liquid is being sprayed on the metal seed layer. In addition, or alternatively, the substrate may be rotated and/or vibrated and/or otherwise agitated while being held in a stationary bath. In addition, or alternatively, the substrate may be processed in a megasonic tank, an ultrasonic tank or the like that contains the pre-cleaning liquid.

The pre-cleaning liquid to which the metal seed layer is exposed may include water, such as deionized water. The pre-cleaning liquid alternatively or additionally may include a surfactant, an etchant and/or an organic solvent.

FIG. 2 is a schematic side view of a conventional megasonic tank 201 in which part or all of the inventive pre-cleaning step 103 may be performed. The megasonic tank 201 includes a tank 203 which holds a liquid 205. The liquid 205 may, for example, be deionized water, or any other type of pre-cleaning liquid referred to above or hereinafter. The liquid 205 may also be any conventional liquid employed in a megasonic tank (e.g., during substrate cleaning).

A substrate 207 (e.g., a silicon wafer on which a copper or other seed layer has been deposited) is supported on one or more rollers 209 so as to be completely or partially submerged in the liquid 205 in the tank 203. One or more of the rollers 209 may be motor driven, so as to

rotate the substrate 207 as indicated, for example, by the arrow 211 in FIG. 2. Alternatively, all of the rollers 209 may be fixed so that the substrate 207 does not rotate.

There may be more or fewer than the three rollers 209 illustrated in FIG. 2. A support or supports for the substrate 207 other than the rollers 209 may be employed.

A transducer 213 is positioned at the bottom of the tank 203. An energizing circuit 215 is coupled to the transducer 213. The energizing circuit 215 drives the transducer 213 so that megasonic and/or ultrasonic energy is transmitted through the liquid 205 to impinge upon the substrate 207, and particularly upon a metal seed layer previously deposited on the substrate 207. The transducer 213 need not be located at the bottom of the tank 203, and two or more transducers may be employed rather than the single transducer 213 shown in FIG. 2.

FIG. 3 is a schematic perspective view of an apparatus 301 that may be employed to perform an agitated rinse during the pre-cleaning step 103 of FIG. 1. In the apparatus 301 a substrate 207 is supported in a horizontal orientation and is rotated by a mechanism which is schematically represented by an arrow 303 (e.g., a rotatable substrate support or other similar mechanism). While the substrate 207 is being rotated, a pre-cleaning liquid 305 is sprayed on the substrate 207, and particularly on a metal seed layer (e.g., a copper seed layer) that has been formed on the substrate 207. The pre-cleaning liquid 305 is sprayed from a nozzle 307 that is connected to a pre-cleaning liquid supply 309. A jet, spray bar or other similar device also may be employed.

The pre-cleaning liquid 305 may be, for example, deionized water, or any other pre-cleaning liquid referred to hereinabove or hereinafter. The substrate 207 may be stationary, rather than in rotation, while the pre-cleaning liquid 305 is sprayed on the substrate 207. As noted above,

the substrate 207 may be vibrated or otherwise agitated while the pre-cleaning liquid 305 is being sprayed thereon. The vibration (or other agitation) of the substrate 207 may or may not occur while the substrate 207 is being rotated.

5           A pre-cleaning liquid that may be employed in step 103 may include, for example, a surfactant. One surfactant that may be employed is sold under the trademark Alfonic®, available from Sasol. For example, the surfactant Alfonic® may be added to the cleaning solution Electra-Clean®  
10 (available from Applied Materials, Inc.), and the resulting solution may be used as a pre-cleaning liquid. Such a solution may comprise, for example, citric acid, ammonium citrate and a surfactant such as ethoxylated alcohol.

          A pre-cleaning liquid for step 103 also may  
15 include an additive suppressor solution for electrochemical plating such as polyethylene glycol. Another solution that may be used as a pre-cleaning liquid in step 103 is sold under the trademark Citrajet®, available from Alconox, Inc. (e.g., citric acid and a surfactant).

20           As indicated above, one or more of the above-referenced pre-cleaning liquids may include citric acid and/or ammonium citrate. Surfactants that may be employed in a pre-cleaning liquid include, for example, ethoxylated alcohol, polyethylene glycol, ethylene oxide/propylene oxide  
25 block copolymers, amine alkoxylates, alkylphenol alkoxylates, and polypropylene glycols. A pre-cleaning liquid may include an organic or other solvent such as acetone, IPA (isopropyl alcohol), hexane, 3M HFE series (e.g., HFE-7100, HFE-7200, HFE-71DE, HFE-71IPA), ethyl  
30 lactate, Fomblin® Perfluorosolv PFS-1, supercritical carbon dioxide, etc. Other pre-cleaning liquid additives may be employed, such as etchants (e.g., citric or other acids), basic-type materials (e.g., tetramethyl ammonium hydroxide (TMAH), ammonium hydroxide or potassium hydroxide or the  
35 like).

The pre-clean step 103 may include one or more sub-steps, in which a substrate is dipped and/or held in a stationary bath, or is subjected to an agitated rinse. The pre-cleaning liquid used in one or more such sub-steps may  
5 be, for example, an etchant, such as an acidic solution (or any of the other pre-cleaning liquids described herein).

Steps 103 and 105 may be performed in separate processing chambers. Alternatively, both steps 103 and 105 may be performed in the same chamber. Step 105 thereby may  
10 be performed immediately following step 103 to reduce/prevent recontamination and/or oxidation of a metal seed layer following pre-cleaning (step 103) but prior to electrochemical deposition (step 105). For example, FIG. 4 is a schematic top plan view of an apparatus 401 in which  
15 such an embodiment of the invention may be performed. The inventive apparatus 401 includes a chamber 403 in which a pre-cleaning station 405 and an electrochemical deposition (ECD) station 407 are located. An arrow 409 schematically represents a mechanism, such as a robotic arm, for  
20 transferring a substrate (not shown) from the pre-cleaning station 405 to the ECD station 407. At the pre-cleaning station 405, one or more of the above-described embodiments of step 103 may be performed. At the ECD station 407, step 105 may be performed in accordance with conventional  
25 practices. There may be an intervening step and/or station included, between pre-cleaning at station 405 and electrochemical deposition at station 407. In the intervening step or station, for example, a rinse in deionized water may occur.

30 The present inventors have found that, with regard to copper contacts, if the inventive pre-clean step 103 is not employed, application of an ECD electrolyte to a copper seed layer may result in a contact or wetting angle in excess of 40° (as is understood by those skilled in the art,  
35 a contact or wetting angle is the angle of the

electrolyte/air interface relative to a surface of the substrate.) This indicates rather poor wettability of the copper seed layer if the pre-clean step 103 is not performed, and the poor wettability may result in an ECD process that leaves a considerable number of voids in the copper fill layer. On the other hand, in certain applications, performance of the inventive pre-clean step 103 prior to electrochemical deposition of the copper fill layer may reduce the contact angle to less than 15°, indicating a significant improvement of wettability. Moreover, in some cases, the performance of the pre-clean step 103 in accordance with the invention has been found to reduce voids that are in excess of one micrometer by 45% to 85%. It is believed that the improvement in wettability and corresponding reduction in voids may be due to the removal of organic contaminants from the copper seed layer.

Applicants have observed that with regard to copper metallization processes, in the absence of the inventive pre-clean step 103, wettability tends to be reduced as the time delay between copper seed layer deposition and subsequent copper fill layer deposition is increased. However, with performance of the inventive pre-clean step 103 shortly before copper fill layer deposition, process limits on waiting (queue) time after the copper seed layer deposition may be relaxed or eliminated. Performing the inventive pre-clean step tends to render a copper seed layer surface hydrophilic (e.g., allowing water and electroplating solution to evenly coat the surface thereby decreasing the wetting angle of the surface). Contaminants tend to render the copper seed layer surface hydrophobic (e.g., causing water and electroplating solution to pool together and not spread evenly, thereby increasing the wetting angle of the surface).

In at least one embodiment of the invention, one or more of the inventive pre-cleaning processes (e.g.,

etching, detergency such as use of surfactants, hydrodynamic impingement and/or other agitated rinsing, etc.) may be performed with an aqueous solution, such as one of the above described pre-cleaning liquids, having a PH between about 1  
5 and 13 and a temperature between about 10 and 90°C. Other PH and/or temperature ranges may be employed.

In a further embodiment of the step 103 referred to above, step 103 may include (or consist of) a pre-cleaning and/or pre-treating step in which the metal seed  
10 layer is exposed to a solution containing an oxidant. Such a solution may form an oxidized layer on the surface of the metal seed layer, which may be even more wettable in an electrolyte solution of an ECD bath than the pure metal surface. As such, wherein providing a clean, pure metal  
15 seed layer surface may be a common goal of one or more embodiments of step 103, in at least one embodiment a further goal may be to pre-treat a metal seed layer so as to increase the wettability of the metal seed layer beyond that of a pure metal surface. The present embodiment of a pre-  
20 clean/pre-treatment may be similar to the embodiments described above. For example, an aqueous (e.g., DI water) solution containing an oxidant may be used, and/or the substrate may be rinsed or dipped in the oxidant-containing aqueous solution, and/or an option may be provided so that  
25 either the same or different chambers may be used for the pre-clean/pre-treatment and the electroplating steps.

In a specific example, the pre-cleaning (and/or pre-treating) solution may include an aqueous solution (e.g., DI water), and the oxidant (e.g., hydrogen peroxide  
30 having a concentration from about .1 percent to about 6 percent). Other concentrations may be employed. Further, the pre-cleaning solution may be substantially free of etching agents, e.g., agents that would tend to etch an oxide layer, such that the hydrogen peroxide may be  
35 permitted to form a layer of metal oxide on the surface of

the metal seed layer. In at least one embodiment, the length of time during which the substrate may be exposed to the oxidant-containing solution may be, for example, about a minute or less (e.g., from about 30 seconds to about 60  
5 seconds). Other time ranges may be employed.

The oxide layer preferably is thin (e.g., about 100 angstroms or less). Such a thin oxide layer may be removed via etching at the onset of electroplating (e.g., thinner oxide layers are more likely to be removed by such  
10 etching). Other oxide layer thicknesses may be employed, including oxide layer thicknesses that are not completely removed during electroplating. Once the desired oxidized layer is formed, the substrate may then be dried (e.g., via spin-rinse drying, and/or impingement of nitrogen gas), and  
15 then immersed in the electrolyte solution of the ECD bath. Such an oxidized layer may serve to decrease the formation of gas bubbles on the surface of the metal seed layer as a result of subsequent immersion of the substrate in the electroplating solution. Reducing an oxidized surface back  
20 to the pure metallic state via etching from the electrolyte solution at the onset of the electroplating process may promote a subsequent deposition that is free of defects.

The above described preparatory formation of an oxidized surface on the metal seed layer prior to immersion  
25 in the electrolyte solution of the ECD bath may be considered compatible with other pre-cleaning steps described herein with respect to the present invention. For example, one or more such pre-cleaning steps may be undertaken before so forming an oxidized surface, and the  
30 surface oxidation layer so formed may be thin enough to be substantially and/or completely eliminated at the outset of the electroplating process.

In addition to or instead of the liquid pre-clean embodiments of step 103 referred to above, step 103 may  
35 include or consist of a dry pre-clean process in which the

metal seed layer is exposed to an activated species such as hydrogen and/or oxygen. For example, activated hydrogen may reduce copper oxide on a copper seed layer, as a result of which water vapor may be formed and exhausted away, and the copper seed layer left free of oxide. An advantage of this process is that the copper oxide is eliminated with little or no reduction in thickness of the copper seed layer. Contaminants also may be removed from the seed layer.

FIG. 5 is a schematic cross-sectional view of a processing apparatus 501 that may be employed for step 103 of FIG. 1 (e.g., for oxide reduction and/or contamination removal by activated hydrogen or the like) in accordance with an embodiment of the invention. For convenience, the processing apparatus 501 will be described with reference to the use of hydrogen and/or oxygen to pre-clean a copper seed layer. It will be understood that other reactive species and other metal and/or seed layers may be similarly pre-cleaned.

The processing apparatus 501 includes a process chamber 503, which may or may not be gas-tight. A pedestal 505 is situated in the process chamber 503 and is adapted to support a substrate 207 during processing in the process chamber 503. A power source (not shown) may be employed to bias the pedestal 505 (and thus the substrate 207) during processing using, for example, DC or RF biasing.

A gas supply 507 and a remote plasma source 509 are coupled to the process chamber 503 for the purpose of providing to the process chamber an activated species such as a hydrogen (or hydrogen/diluent gas) plasma. In particular, the gas supply 507 is coupled to the remote plasma source 509 via a first gas line 511 and the remote plasma source 509 is coupled to the process chamber 503 by a second gas line 513. In at least one embodiment, the gas supply 507 is a source of hydrogen gas, or a gas that is a mixture of hydrogen and another gas, such as argon or



nitrogen. The remote plasma source 509 may be provided in accordance with conventional principles and may, for example, form a plasma of the gas supplied from the gas supply 507 by microwave excitation. The resulting plasma  
5 generated in the remote plasma source 509 is conducted via the second gas line 513 to the process chamber 503.

Although not shown in FIG. 5, it should be understood that a slit valve or the like may be provided in the process chamber 503 to allow for transfer of the  
10 substrate 207 into and out of the process chamber 503. There may be associated with the process chamber 503 an exhaust system 515 (shown in phantom) for exhausting gases, including process by-products, from the process chamber 503. There may also be included in the process chamber 503 an  
15 arrangement to strike and/or maintain a plasma in the process chamber 503 (e.g., a suitable cathode and/or anode, parallel plates, etc.). If such an in-situ plasma arrangement is provided, the remote plasma source 509 need not be employed.

20 In one exemplary operation, a gas which is or includes hydrogen is supplied to the remote plasma source 509 from the gas supply 507 via the first gas line 511. At the remote plasma source 509, the gas supplied from the gas supply 507 is excited into a plasma (e.g., forming atomic  
25 hydrogen having an energy level above its ground state, missing an electron or otherwise in an ionic state or that is otherwise "activated"). The resulting plasma flows through the second gas line 513 to the process chamber 503. In the process chamber 503, a copper seed layer (not shown)  
30 on the substrate 207 is exposed to the plasma. Copper oxide in the copper seed layer is reduced to copper by hydrogen ions in the plasma (e.g., such as via the reaction  $\text{CuO} + 2\text{H} \rightarrow \text{Cu} + \text{H}_2\text{O}$ ). The resulting water vapor is exhausted from the process chamber 503.

The exposure of the copper seed layer to the hydrogen plasma may also result in removal of contaminants on the copper seed layer. For example, hydrogen ions may combine with organic contaminants to form methane and water vapor, which also may be exhausted from the process chamber 503. Thus the dry pre-clean performed with the processing apparatus 501 may serve to both remove contaminants and reduce/remove copper oxide for a copper seed layer.

In one or more embodiments of the invention, during the exposure of a copper seed layer to a hydrogen, oxygen, or other plasma or other activated species source, the pressure in the process chamber 503 is maintained at or above about 0.1 atmosphere. For example in at least one embodiment, pressures in the range 0.1 to 1 atmosphere may be employed, and in another embodiment the pressure is substantially one atmosphere. Other pressure ranges may be employed.

In previously proposed processes, reduction of copper oxide by a hydrogen plasma has been performed at low pressures, such as a few Torr or less. As has now been recognized, performing hydrogen plasma reduction of copper oxide at a relatively high pressure (e.g., at or above about 0.1 atmosphere or 76 Torr) may allow a simpler and less expensive processing apparatus to be employed. For example, and particularly if the process is performed at or near atmospheric pressure, it may be possible to perform hydrogen plasma reduction without requiring the use of a vacuum pump and/or a vacuum chamber. That is, the process chamber 503 need not be constructed so as to resist the physical demands of maintaining a vacuum.

To obtain an effective reduction of copper oxide in (and particularly on sidewalls of) features such as trenches and vias, a suitable combination of process duration, pressure, hydrogen (or other activated species) concentration, temperature and pedestal bias may be

provided. For example, introduction of a plasma into the process chamber 503 from a remote plasma source, with zero pedestal bias, may reduce directionality of the process (e.g., by reducing directionality with which plasma ions strike a substrate supported by the pedestal 505), so that reduction of copper oxide on via side walls is promoted. It is also noted that low or zero pedestal bias may promote copper oxide reduction by reducing any sputtering effects. It will be understood, however, that a combination of oxide reduction and sputtering may be employed through appropriate pedestal biasing.

In one exemplary embodiment of the invention, a hydrogen plasma is employed to reduce copper oxide using a hydrogen concentration of about 0.5% to 4% (in nitrogen), a chamber pressure of about 2 to 760 Torr, a substrate temperature of about 15 to 150 °C, and a pedestal bias of about 0 to 200 Watts (RF) for a duration of about 20 to 80 seconds. Other processing parameters may be employed.

As an alternative (or in addition) to a hydrogen or hydrogen-containing plasma, hydrogen (or other species) may be activated by exposure to ultraviolet light, or thermally (e.g., by using a substrate temperature of about 400°C or more) and/or chemically. If a plasma is employed, RF, microwave or similar generation of the plasma is contemplated. In at least one embodiment of the invention, the reduction process may be performed at room temperature or higher (e.g., about 20 to 100°C).

As an alternative to the one-step dry pre-cleaning process described above, a two-step process may be employed. For example, a copper seed layer may be exposed to activated oxygen (e.g., an oxygen or oxygen-containing plasma) to remove organic (or other) contaminants, and then the copper seed layer may be exposed to the above-described activated hydrogen to reduce the copper oxide in the copper seed layer. If such a two-step process is to be employed, the

gas supply 507 may include a source of oxygen or oxygen-containing gas in addition to hydrogen or hydrogen-containing gas. In some instances, exposure to oxygen or oxygen-containing plasma or other activated oxygen may  
5 increase copper oxide thickness, thereby requiring a lengthier copper oxide reduction step. In one embodiment, the activated oxygen process is performed at a temperature of about 100°C and the subsequent activated hydrogen process is performed at a temperature of about 20 to 100°C. Other  
10 ranges may be employed.

A dry-pre-clean process in accordance with the invention may eliminate copper oxide from a copper seed layer without significantly decreasing the thickness of the copper seed layer. Consequently, copper contacts which  
15 result therefrom may have reduced resistivity. Moreover, since the copper seed layer is not significantly thinned by the oxide reduction process, a relatively thin seed layer may be employed, thereby decreasing process time and increasing throughput. Further, since the present invention  
20 provides for dry pre-cleaning at a relatively high pressure, an apparatus employed to perform the dry pre-cleaning process may be simple and inexpensive (e.g., a non-vacuum chamber), thereby reducing manufacturing costs. In addition, the dry pre-cleaning process may reduce  
25 contamination on a metal seed layer, thereby improving wettability at an electrochemical deposition (ECD) stage. Accordingly, a number of voids resulting from ECD may be reduced.

It should also be noted that the inventive dry  
30 pre-cleaning process, in addition to improving results obtained in filling features such as trenches and vias, may also improve uniformity and efficiency of an ECD step, by reducing copper oxide at the edges of the substrate 207 (thereby improving electrical contact during ECD).

The foregoing description discloses only exemplary embodiments of the invention; modifications of the above disclosed apparatus and methods which fall within the scope of the invention will be readily apparent to those of  
5 ordinary skill in the art. For example, although the present invention has been described in conjunction with pre-cleaning a copper seed layer in preparation for ECD of a copper fill layer, it also may be employed with other processes (e.g., metallization with aluminum or other metals  
10 or similar materials). Any combination of liquid pre-cleaning methods may be employed (e.g., agitated rinsing, use of surfactants, etchants, solvents, oxidants, etc., or the like), sequentially or simultaneously, as may a combination of wet and dry pre-cleaning.

15 Accordingly, while the present invention has been disclosed in connection with exemplary embodiments thereof, it should be understood that other embodiments may fall within the spirit and scope of the invention, as defined by the following claims.